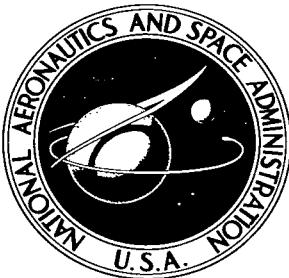


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EXPANSION AND FLOW CHARACTERISTICS OF INITIALLY SATURATED SODIUM, POTASSIUM, AND CESIUM VAPORS

by Louis J. Goldman

*Lewis Research Center
Cleveland, Ohio*



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SUMMARY

An analysis was conducted to determine the type of expansion occurring during the flow of an alkali-metal vapor through a convergent-divergent nozzle. Previously obtained experimental nozzle pressure profile and critical weight-flow data at temperatures of 1200° to 1600° F for sodium vapor and potassium vapor were compared with three idealized processes (equilibrium, supersaturated-equilibrium chemical species, and supersaturated-frozen chemical species) to determine the process that best represents the data. Experimental high-temperature thermodynamic properties were used to perform the theoretical calculations. A simplified theory of nucleation was then applied to both supersaturated processes to give a further insight into the process occurring. In addition, the theoretical expansion, flow, and nucleation characteristics of cesium vapor are presented.

The experimental data for both sodium and potassium were best represented by the supersaturated-equilibrium chemical species process. Calculations for the supersaturated-equilibrium chemical species process indicated that this process could be approximated by the equation $Pv^n = c$, where P is the absolute pressure, v is the specific volume, n is the expansion index, and c is a constant. The theoretical expansion index values of 1.35 and 1.44 for the supersaturated-equilibrium chemical species process for sodium vapor and potassium vapor, respectively, are recommended for design calculations. The nucleation characteristics for the supersaturated-equilibrium chemical species process for sodium and potassium differed significantly from those for the frozen process and indicated the possibility of a condensation-free expansion for these fluids. The decreased heat released during the supersaturated-equilibrium chemical species expansion for cesium results in expansion, flow, and nucleation characteristics that do not differ significantly from those for a frozen process. A condensation-free expansion for cesium appears less likely than for either sodium or potassium.

INTRODUCTION

A knowledge of the expansion and flow characteristics of alkali-metal vapors is required for the proper design of turbines for use in the Rankine cycle space power systems. With this information lacking, the usual practice is to use one of the two flow-limiting processes (equilibrium and supersaturated-frozen) as the basis for the design. In the equilibrium process, the expansion is assumed to occur with equilibrium both between the physical phases of vapor and liquid and between the chemical species of monomer, dimer, etc., in the vapor phase. In the supersaturated-frozen process, it is assumed that neither condensation of the vapor nor reaction between the chemical species occurs during the expansion. The flow characteristics for these two processes differ significantly; for example, about 10 percent more flow can pass through a given area for the supersaturated-frozen process. Therefore, a better identification of the process is required.

To identify the expansion process better, an experimental program was conducted at the NASA Lewis Research Center. Nozzle-pressure profiles and critical weight-flow rates through a convergent-divergent nozzle were measured for sodium vapor and potassium vapor at temperatures of 1200° to 1600° F. The two-phase flash vaporization facility described in reference 1 was employed to generate the vapors. The experimental results are presented in references 2 to 4.

In general, neither of the two flow-limiting processes represented the experimental data. A supersaturated-equilibrium chemical species process, wherein the vapor is supersaturated but the molecular species are in equilibrium, was proposed (ref. 4) to represent the potassium data best. For sodium, a lack of experimental high-temperature thermodynamic properties at the time of the investigation precluded identification of the expansion process.

The objectives of this report are: (1) to determine if the experimental data for sodium could also be represented by the supersaturated-equilibrium chemical species process, (experimental high-temperature thermodynamic data have made such a determination possible) and (2) to examine the compatibility of the supersaturated-equilibrium chemical species process with the nucleation theory of condensation.

The experimental results for initially saturated sodium vapor and potassium vapor (refs. 2 to 4) are summarized herein and reevaluated by using more definitive experimental high-temperature thermodynamic properties. The nucleation characteristics for the supersaturated-equilibrium chemical species process are presented and compared with the nucleation characteristics for a frozen process (ref. 5). Finally, the theoretical expansion, flow, and nucleation characteristics of cesium vapor are presented.

SYMBOLS

A	area, ft ²
C _p	molal specific heat at constant pressure, Btu/(lb-mole)(⁰ R)
C _v	molal specific heat at constant volume, Btu/(lb-mole)(⁰ R)
c	constant
g	acceleration of gravity, 32.17 ft/sec ²
J	mechanical equivalent of heat, 778.2 ft-lb/Btu
J*	nucleation rate, nuclei/sec-ft ³
k	Boltzmann constant, 5.652×10 ⁻²⁴ ft-lb/ ⁰ R
M	molecular weight of monomer, lb/lb-mole
N	Avogadro's number, 2.732×10 ²⁶ molecules/lb-mole
n	expansion index
P	absolute pressure, lb/ft ²
R	universal gas constant, 1545 ft-lb/(lb-mole)(⁰ R)
r*	radius of condensation nucleus, ft
T	temperature, ⁰ R
V	velocity, ft/sec
v	specific volume, ft ³ /lb
W	weight-flow rate, lb/sec
ρ_l	density of liquid, lb/ft ³
σ	surface tension, lb/ft
Subscripts:	
f	frozen
P	pressure
s	entropy
sat	saturated state
T	temperature
t	throat of nozzle
x	variable state point
0	inlet of nozzle

ANALYSIS

Expansion Processes

When an initially saturated vapor expands through a nozzle, an equilibrium state generally does not exist during all phases in the expansion process. An unstable or supersaturated state (undercooling of a vapor below its saturation temperature without condensation) is likely to exist for at least a portion of the expansion. The extent to which the supersaturated state persists depends on, among other things, the physical and chemical nature of the vapor and the rapidity of the expansion. The point of condensation or the reversion to the equilibrium state can, for given conditions, be theoretically estimated from classical nucleation theory considerations. If the point of condensation occurs at the inlet of the nozzle, an equilibrium process results. On the other hand, if condensation is delayed such that the point of condensation does not occur within the nozzle, a supersaturated expansion process results. These limiting processes are often used, since theoretical calculations for them can be made more conveniently.

For the alkali-metal vapors, the supersaturated state is further complicated by the existence of monomer, dimer, and higher order polymer species in the vapor phase. The concentration of these species during the expansion depends on the kinetic rates of the polymerization reactions. In the absence of this information, it is usually assumed that the rates are either extremely slow or extremely fast. For the extremely slow kinetic rate, the composition of the vapor is frozen at its initial value throughout the expansion and will be referred to as a supersaturated-frozen chemical species process. For the extremely fast kinetic rate, the composition of the vapor changes continuously during the expansion and is determined by the equilibrium constants for the polymerization reactions; this type of expansion will be referred to as a supersaturated-equilibrium chemical species process. For the alkali metals, therefore, three idealized processes are of interest in this analysis: (1) equilibrium, (2) supersaturated-equilibrium chemical species, and (3) supersaturated-frozen chemical species.

Calculation of Process Characteristics

Theoretical expansion and flow. - The theoretical expansion and flow characteristics for the three idealized processes (equilibrium, supersaturated-equilibrium chemical species, and supersaturated-frozen chemical species) have been calculated by assuming one-dimensional, isentropic flow. The experimental high-temperature thermodynamic properties of references 6 to 8 were used for these calculations. The properties were extrapolated slightly to the lower temperatures used in this report.

The maximum or critical weight-flow rate W/A_t can be determined from the continuity equation

$$\frac{W}{A_x} = \frac{V_x}{v_x} \quad (1)$$

by calculating V_x/v_x for various pressure ratios P_x/P_0 and locating the maximum value. The corresponding area ratio A_x/A_t is calculated from the equation

$$\frac{A_x}{A_t} = \frac{\frac{W}{v_x}}{\frac{W}{V_x}} \quad (2)$$

for the selected pressure ratios. The area ratio and the pressure ratio can then be used to obtain the pressure variation through the nozzle.

For the equilibrium process, the velocity V_x is calculated by methods that employ the thermodynamic functions of enthalpy and entropy. The specific volume v_x in this case is calculated for the vapor-liquid mixture. The calculations indicated that the equilibrium process could be approximated by an expansion following the equation $Pv^n = c$. The computational procedure for the equilibrium process is given in reference 1.

For the supersaturated-frozen chemical species process, it is assumed that the vapor behaves as a perfect gas during the expansion. This is equivalent to assuming that molecular weight changes due to the polymerization reactions are the only factors contributing to the nonideality of the alkali-metal vapors. The velocity V_x and the specific volume v_x can be calculated once the expansion index is known. For the preceding assumptions, the expansion index is the ratio of the frozen specific heats $(C_p)_f/(C_v)_f$ and can be determined as described in reference 4.

For the supersaturated-equilibrium chemical species process, the specific volume is obtained from the virial equation of state given in references 6 to 8 once the variation of pressure and temperature during the expansion is known. This variation can be obtained from the thermodynamic relation

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{J}{M} \left(\frac{C_p}{T}\right) \left(\frac{\partial T}{\partial v}\right)_P \quad (3)$$

by numerical integration. The velocity is then calculated from the equation

$$v_x = \left[2g \left(P_0 v_0 - P_x v_x + \int_{v_0}^{v_x} P dv \right) \right]^{1/2} \quad (4)$$

The calculation procedure is also described fully in reference 4.

The results of these calculations indicated that the supersaturated-equilibrium chemical species process could also be approximated by an expansion following the equation $Pv^n = c$ (see appendix). The expansion and flow characteristics can therefore be made more conveniently once the value of n is determined. The expansion index n is calculated from the relation

$$n = - \frac{\frac{v}{P}}{\left(\frac{\partial v}{\partial P} \right)_T + \frac{MT}{JC_p} \left(\frac{\partial v}{\partial T} \right)_P^2} \quad (5)$$

where the derivatives are determined from the virial equation of state at the nozzle inlet.

Nucleation. - The nucleation theory of condensation has been applied to study the expansion behavior of the alkali-metal vapors (ref. 5) by assuming that the chemical species were in a frozen state. The temperature range of this study was from 2000° to 2500° R. In general, the theory predicted condensation upstream of the nozzle throat and, within a fairly narrow range of nucleation rates J^* . A simplified procedure was therefore proposed for estimating the condensation pressure ratio based on a nucleation-rate criterion.

For the supersaturated-equilibrium chemical species process, the direction of the polymerization reactions occurring during the expansion (from monomer to higher order species) are such that heat is continuously being released. This resulting heat effect would therefore tend to delay the point of condensation in comparison with those calculated by assuming a frozen process. The magnitude of this delay could be obtained by performing a condensation analysis similar to that of reference 5 but for an assumed supersaturated-equilibrium chemical species process. Since such an analysis would be complex, the simplified procedure based on a nucleation-rate criterion has been used to estimate the onset of condensation for the supersaturated-equilibrium chemical species process. Such a procedure can serve as a guide in determining if a more rigorous condensation analysis would give significantly different results in comparison with the results for the frozen process.

The nucleation rate J^* is calculated from the equation (ref. 5)

$$J^* = \frac{P^2 M}{N \rho_\ell (kT)^2} \sqrt{\frac{2\sigma g N}{\pi M}} e^{-4\pi\sigma r^*^2/3kT} \quad (6)$$

where the radius of the condensation nucleus r^* is

$$r^* = \frac{2\sigma M}{\rho_\ell R T \ln\left(\frac{P}{P_{\text{sat}}}\right)} \quad (7)$$

The surface tension σ is obtained as in reference 5 by extrapolation of available data at the melting point. Since the surface tension appears to the third power in the nucleation rate equation, small errors in σ are magnified in calculating J^* .

EXPANSION PROCESS IDENTIFICATION

To determine the process that best represents the expansion and flow characteristics of alkali-metal vapors through nozzles, the experimental variation in pressure ratio, expansion index, and critical weight-flow rate data for sodium vapor and potassium vapor (refs. 2 to 4) are compared with the three idealized processes. The nucleation characteristics for the two supersaturated processes are then discussed.

Nozzle-Pressure Profiles

The variation of pressure ratio through the nozzle for sodium vapor and potassium vapor is presented in figure 1. At each measurement location, the average pressure ratio for all nozzle inlet conditions is shown. For sodium, the nozzle inlet pressure ranged from 6.27 to 12.41 pounds per square inch absolute and for potassium from 6.02 to 17.88 pounds per square inch absolute. The theoretical processes are represented by dashed lines. For both fluids, the experimental data are best represented by the supersaturated-equilibrium chemical species process.

Expansion Indexes

The variation of the expansion index n with nozzle inlet temperature for sodium

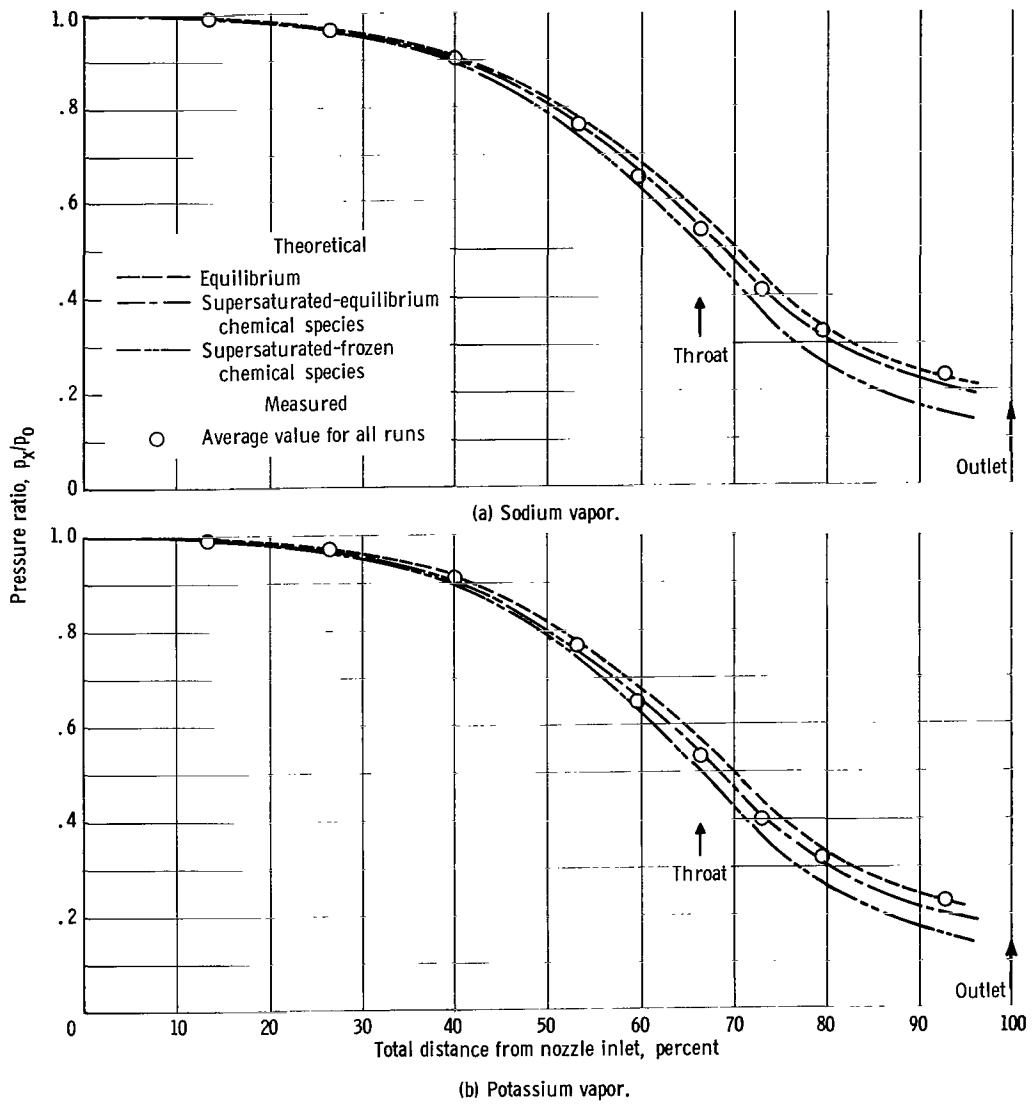


Figure 1. - Variation of static-to inlet-pressure ratio along nozzle wall.

vapor and potassium vapor is shown in figure 2. The experimental expansion indexes were obtained from the nozzle pressure data by employing the graphic least-squares technique described in reference 2. The theoretical expansion indexes for the three idealized processes were calculated by assuming the expansions follow the equation $Pv^n = c$. The experimental expansion indexes for both fluids are best represented by the $Pv^n = c$ approximation of the supersaturated-equilibrium chemical species process. The theoretical values of the expansion index in the temperature range of this report are about 1.35 and 1.44 for sodium vapor and potassium vapor, respectively. The experimental expansion index, as plotted in figure 2, includes the effect of friction in the nozzle. It is estimated that the friction has decreased the experimental expansion index by about 2 percent.

Critical Weight-Flow Rates

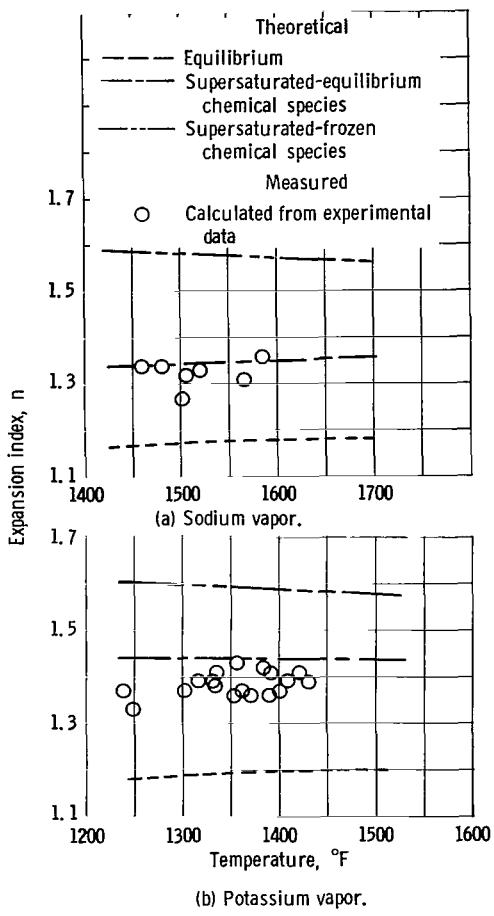


Figure 2. - Variation of expansion index with nozzle-inlet temperature.

Constant nucleation rates J^* of 10^{20} and 10^{25} , which were shown in reference 5 to bracket approximately the predicted condensation pressure ratios in the temperature range of 2000° to 2500° R, are represented by dashed lines. In the lower temperature range of this report (1700° to 2100° R), the condensation pressure ratios for the frozen process occur at nucleation rates slightly higher than 10^{25} .

For sodium vapor (fig. 4(a)), the pressure ratios for the supersaturated-equilibrium chemical species process at a nucleation rate of 10^{20} occurred downstream of the nozzle throat. A nucleation rate of 10^{25} for the supersaturated-equilibrium chemical species process did not occur for the lowest calculated pressure ratio, which was 0.1 and is not shown in the figure. It is concluded that the heat released during the supersaturated-

The variation of the critical weight-flow rate with nozzle inlet pressure for sodium vapor and potassium vapor is presented in figure 3. For runs made at the same inlet conditions, the average value of the weight-flow rate is plotted. The experimental flow rates have been corrected for a nozzle flow coefficient of 0.97, which was determined by air pretests. Comparison of the experimental flows with flows for the theoretical processes indicates that the data are best represented by the supersaturated-equilibrium chemical species process. This comparison is made by assuming that the vapors entering the nozzle are saturated. Although energy-balance calculations indicated qualities better than 98 percent, slight deviations within this 2-percent range could possibly explain some of the data scatter noted in the figures.

Nucleation Considerations

The nucleation characteristics for sodium vapor and potassium vapor are presented in figure 4. The condensation pressure ratios predicted by nucleation theory for the frozen process (ref. 5) are represented by the solid line in this figure.

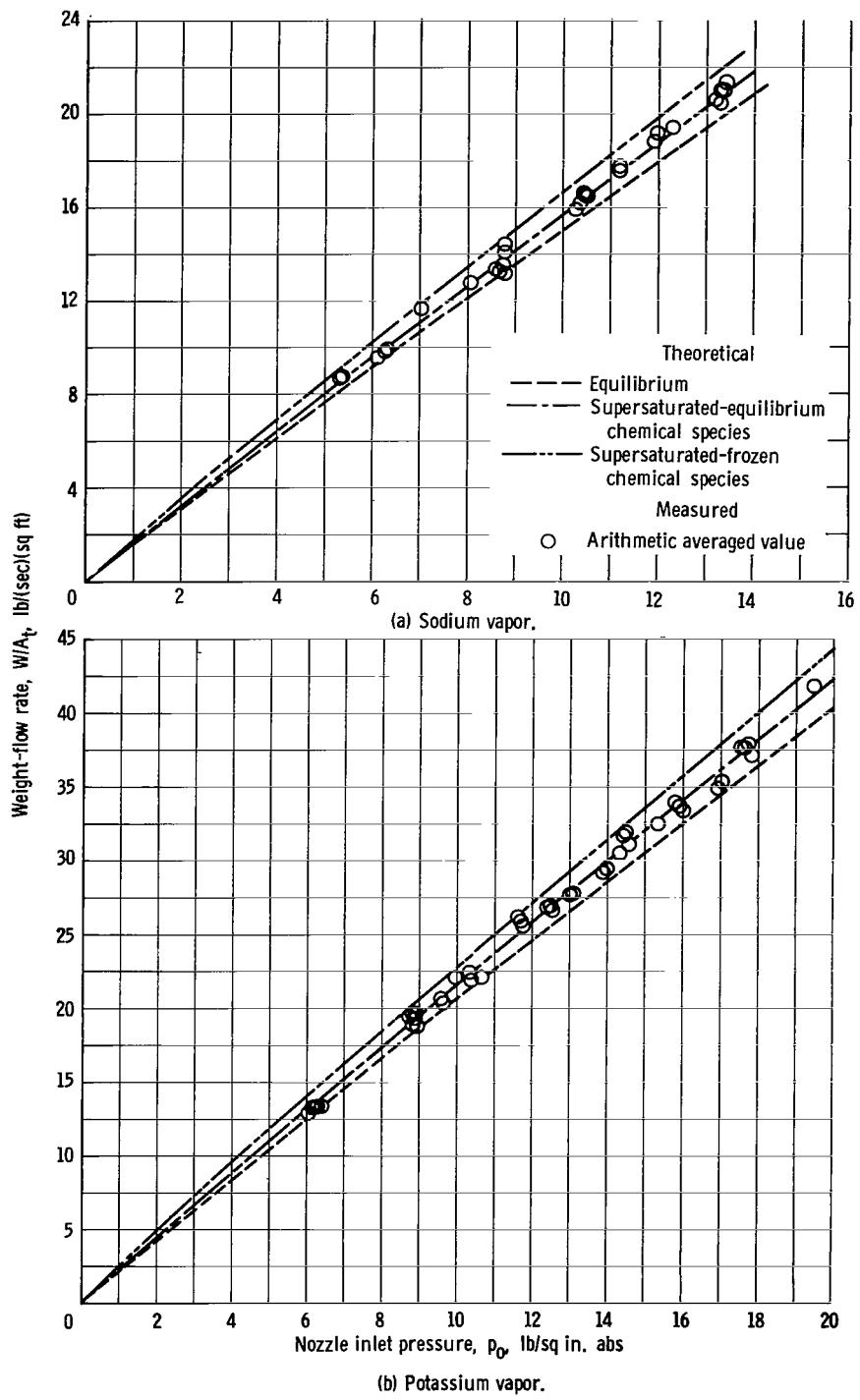


Figure 3. - Variation of critical weight-flow rate with nozzle-inlet pressure.

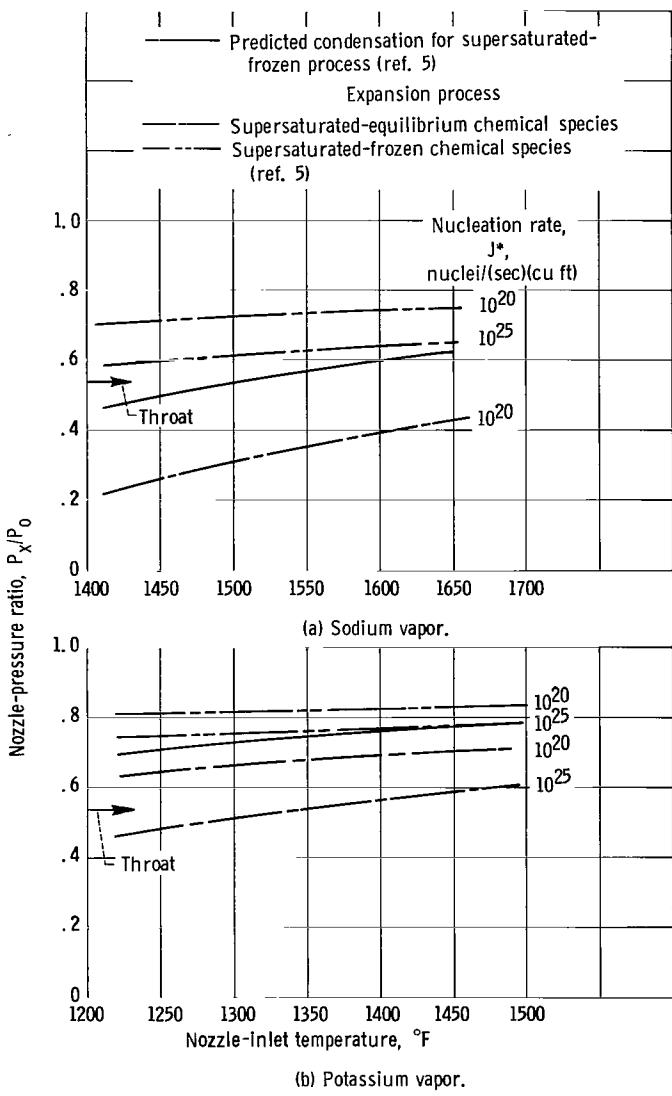


Figure 4. - Variation of nozzle-pressure ratio with nozzle-inlet temperature for values of nucleation rate.

equilibrium chemical species expansion significantly affects the nucleation rate, and therefore condensation-free expansion may be possible for sodium vapor.

For potassium vapor (fig. 4(b)), the pressure ratios for the supersaturated-equilibrium chemical species process at nucleation rates of 10^{20} and 10^{25} occur upstream and in the vicinity of the nozzle throat, respectively. A nucleation rate of 10^{30} did not occur for pressure ratios as low as 0.1 in this process. If condensation is delayed until nucleation rates slightly greater than 10^{25} occur, condensation-free expansion would also be possible for potassium vapor.

THEORETICAL EXPANSION AND FLOW CHARACTERISTICS OF CESIUM VAPOR

The theoretical expansion and flow characteristics of cesium vapor are presented in figures 5 to 7. To be consistent, the same type of figures are shown for cesium as were shown for sodium and potassium. For simplicity, the calculations for the supersaturated-equilibrium chemical species process were performed by assuming that the expansion follows the equation $Pv^n = c$. The expansion indexes for the three processes for cesium are shown in figure 5; the proximity of the expansion indexes for the two supersaturated processes is also noted. In fact, comparison of the expansion indexes of sodium (fig. 2(a)) and potassium (fig. 2(b)) for the two supersaturated processes indicates that the supersaturated-equilibrium chemical species process approaches the supersaturated-frozen chemical species process as the molecular weight of the alkali metal increases. This increasing proximity of the supersaturated processes results from the decreasing heat released during the polymerization reaction as the molecular weight increases. Typical values of the expansion index for cesium at 1300°F , for example, are 1.21, 1.50, and 1.58 for the equilibrium process, the supersaturated-equilibrium chemical species process, and the supersaturated-frozen chemical species process, respectively. Because of the small quantity of heat released during the polymerization reaction, the pressure variation (fig. 6) and the critical weight-flow (fig. 7) for the two supersaturated processes do not differ significantly for cesium.

The nucleation characteristics for cesium vapor are presented in figure 8. Because of the decreased heat released during the polymerization reaction for cesium, the nucleation rates for the supersaturated-equilibrium chemical species process do not differ significantly from the nucleation rates for the frozen process. A nucleation rate of 10^{25} occurs well upstream of the nozzle throat. For the nucleation theory to predict condensation-free expansion for cesium, either condensation would have to be delayed until nucleation rates significantly greater than 10^{25} have occurred, or the actual value of the surface tension would have to be considerably larger than the extrapolated value used in this report.

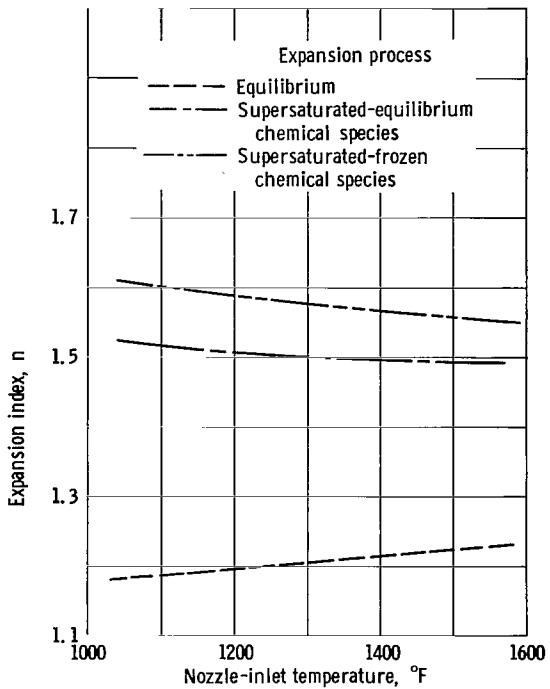


Figure 5. - Variation of expansion index with nozzle-inlet temperature for cesium vapor.

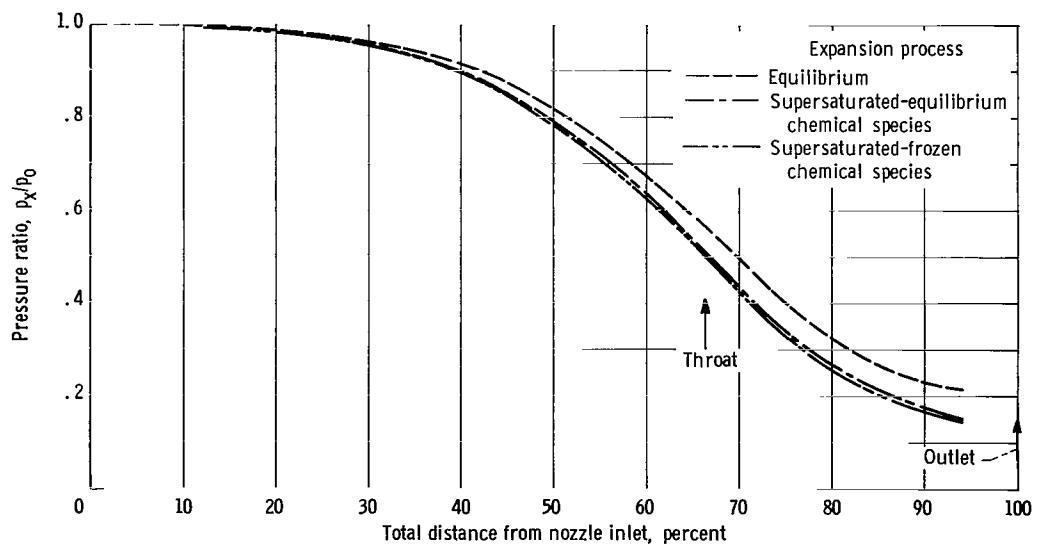


Figure 6. - Variation of static-to inlet-pressure ratio along nozzle wall for cesium vapor.

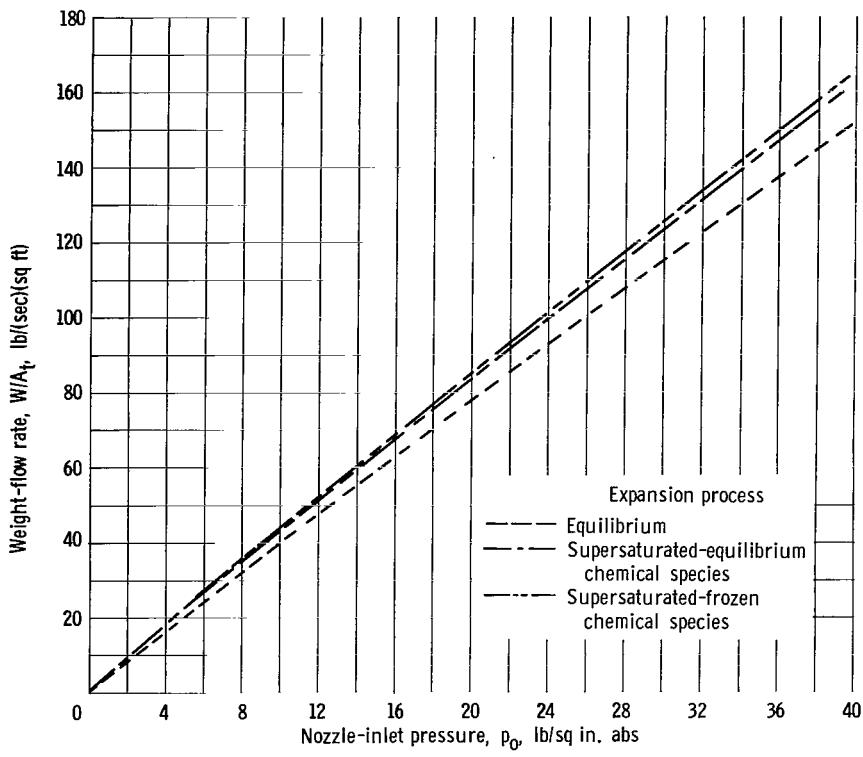


Figure 7. - Variation of critical weight-flow rate with nozzle-inlet pressure for cesium vapor.

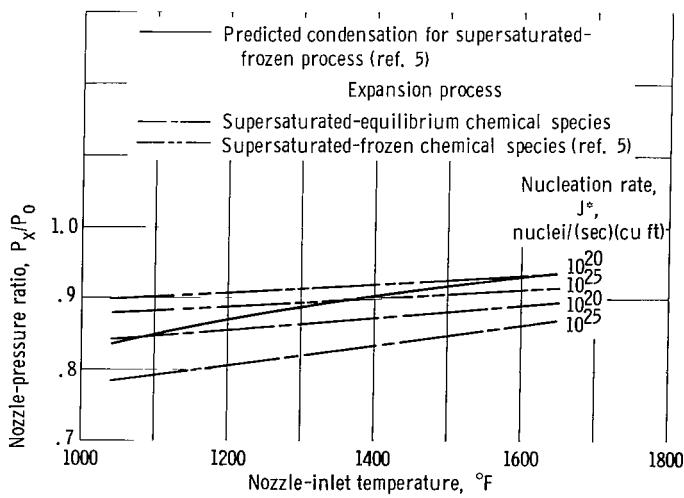


Figure 8. - Variation of nozzle-pressure ratio with nozzle-inlet temperature for values of nucleation rate in cesium vapor.

CONCLUSIONS

An analysis was conducted to determine the type of expansion process occurring during the flow of an alkali-metal vapor through a convergent-divergent nozzle. Previously obtained experimental nozzle pressure profile and critical weight-flow data at temperatures of 1200° to 1600° F for sodium vapor and potassium vapor were compared with three idealized theoretical processes (equilibrium, supersaturated-equilibrium chemical species, and supersaturated-frozen chemical species). The calculations for the theoretical processes were performed by using experimental high-temperature thermodynamic properties. The nucleation characteristics for the supersaturated-equilibrium chemical species process are also presented and compared with the nucleation characteristics obtained for the frozen process. In addition, the theoretical expansion and flow characteristics of cesium vapor have been presented. The following conclusions were reached:

1. For both sodium vapor and potassium vapor, the experimental nozzle-pressure profiles and critical weight-flows were best represented by a supersaturated-equilibrium chemical species process.
2. Calculations for the supersaturated-equilibrium chemical species expansion indicated that this process could be approximated by $Pv^n = c$, where P is the absolute pressure, v is the specific volume, n is the expansion index, and c is a constant.
3. The theoretical expansion index values n of 1.35 and 1.44 for the supersaturated-equilibrium chemical species process for sodium vapor and potassium vapor, respectively, are recommended for design calculations and compared favorably with those obtained experimentally.
4. For cesium vapor, the theoretical expansion indexes at 1300° F for the equilibrium process, the supersaturated-equilibrium chemical species process, and the supersaturated-frozen chemical species process are 1.21, 1.50, and 1.58, respectively.
5. The heat released during the supersaturated-equilibrium chemical species expansion for sodium and potassium significantly delayed the nucleation rates in comparison with the nucleation rates for the frozen process. Condensation-free expansion for these fluids would therefore appear possible.
6. The decreased heat released during the supersaturated-equilibrium chemical species process for cesium results in expansion, flow, and nucleation characteristics that do not differ significantly from those for a frozen process. A condensation-free expansion for cesium appears less likely than for either sodium or potassium.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 31, 1966,
120-27-04-04-22.

APPENDIX - COMPARISON OF SUPERSATURATED-EQUILIBRIUM CHEMICAL SPECIES PROCESS WITH $Pv^n = c$ PROCESS

The theoretical calculation of the expansion and flows characteristics for the supersaturated-equilibrium chemical species process is rather complicated and time consuming, so that a simplified procedure would be valuable. The calculations become straightforward if it is assumed that the expansion follows the equation $Pv^n = c$. The pressure variation and the critical weight-flow for the rigorous supersaturated-equilibrium chemical species process and the $Pv^n = c$ process are compared in tables I and II. With the exception of pressure ratio downstream of the nozzle throat, the supersaturated-equilibrium chemical species process can be approximated by an expansion following the equation $Pv^n = c$.

TABLE I. - PRESSURE VARIATION FOR SUPERSATURATED-EQUILIBRIUM CHEMICAL SPECIES AND $Pv^n = c$ PROCESSES

Vapor											
Sodium						Potassium					
Nozzle inlet temperature, T_0 , $^{\circ}$ R											
1920			2060			1710			1890		
Pressure ratio, P_x/P_0	Deviation from supersaturated-equilibrium chemical species, percent	Pressure ratio, P_x/P_0	Deviation from supersaturated-equilibrium chemical species, percent	Pressure ratio, P_x/P_0	Deviation from supersaturated-equilibrium chemical species, percent	Pressure ratio, P_x/P_0	Deviation from supersaturated-equilibrium chemical species, percent	Pressure ratio, P_x/P_0	Deviation from supersaturated-equilibrium chemical species, percent	Pressure ratio, P_x/P_0	Deviation from supersaturated-equilibrium chemical species, percent
Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$	Supersaturated- $Pv^n = c$
0.970	0.970	0.0	0.970	0.970	0.0	0.968	0.969	0.1	0.969	0.969	0.0
.907	.908	.1	.906	.908	.2	.903	.904	.1	.903	.904	.1
.764	.763	-.1	.762	.762	.0	.757	.753	-.5	.757	.753	-.5
.668	.663	-.7	.664	.662	-.3	.659	.649	-1.5	.659	.650	-1.4
.548	.538	-1.8	.543	.537	-1.1	.539	.522	-3.2	.537	.522	-2.8
.418	.403	-3.6	.413	.401	-2.9	.408	.384	-5.9	.406	.385	-5.2
.317	.298	-6.0	.312	.296	-5.1	.307	.281	-8.5	.306	.281	-8.2
.209	.188	-10.0	.204	.186	-8.8	.200	.172	-14.0	.199	.173	-13.1

TABLE II. - CRITICAL WEIGHT-FLOW VARIATION FOR
 SUPERSATURATED-EQUILIBRIUM CHEMICAL
 SPECIES AND $Pv^n = c$ PROCESSES

Nozzle inlet temperature, T_0 , $^{\circ}$ R	Critical weight-flow, W/A_t , lb/(sec)(sq ft)		Deviation from supersaturated- equilibrium chemical species, percent
	Supersaturated- equilibrium chemical species	$Pv^n = c$	
Sodium			
1920	9.849	9.927	0.8
1965	12.683	12.771	.7
2010	16.149	16.239	.6
2060	20.857	20.940	.9
Potassium			
1710	14.478	14.728	1.7
1765	19.799	20.118	1.6
1800	23.921	24.287	1.5
1815	25.883	26.268	1.5

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